

PATENT SPECIFICATION

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(54) PRODUCING SULFUR DIOXIDE AND OXYGEN FROM SULFUR TRIOXIDE

(71) We, WESTINGHOUSE ELECTRIC CORPORATION of Westinghouse Building, Gateway Center, Pittsburgh, Pennsylvania, United States of America, a company organised and existing under the laws of the Commonwealth of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the production of sulfur dioxide and oxygen from sulfur trioxide.

The demands on electric power plants are cyclical, peaking during the day and diminishing during the night. More efficient use can be made of the facilities if power produced in off hours can be stored for use during peak hours.

One way to accomplish this is to use energy produced during the off hours to decompose water into hydrogen and oxygen, producing a clean, easily stored fuel. Many of the processes which decompose water use as one step in the process the decomposition of sulfur trioxide into sulfur dioxide and oxygen. That reaction proceeds without a catalyst but the reaction rate is low and the reaction time is long.

The reduction of sulfur trioxide into sulfur dioxide using magnetite is disclosed in an article titled "The Reduction of Sulfur Trioxide By Constituents Of Boiler Flue Dust" by H. E. Crossley, A. Poll, and F. Swett in The Institute Of Fuel, April 1968, pages 206 to 213.

According to the present invention a method for the net conversion of gaseous sulfur trioxide into sulfur dioxide and oxygen according to the equation $2\text{SO}_3 \longrightarrow 2\text{SO}_2 + \text{O}_2$ comprises passing said gaseous sulfur trioxide over a sulfuric acid contact catalyst at a temperature of 750 to 1000°C at a space velocity (as hereinafter defined) of at least 100 hr^{-1} ; and preventing sulfur dioxide and oxygen produced from contacting said catalyst at a temperature of less than 750°C.

It has been discovered that sulfuric acid contact catalysts greatly facilitate the decomposition of sulfur trioxide, but only when they are heated to 750 to 1000°C.

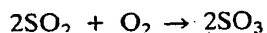
Equilibrium conversion of SO_3 to SO_2 and O_2 is effected at space velocities of at least 10,000 hr^{-1} which is a relatively high space velocity for equilibrium conversion compared to most chemical reactions.

In order that the invention can be more clearly understood, a convenient embodiment thereof will now be described, by way of example, with reference to the accompanying drawing in which:

Figure 1 is a diagram of apparatus for performing the process of this invention.

In Figure 1 liquid SO_3 from line 1 is heated in evaporator 2 to produce gaseous SO_3 in line 3. A valve 4 controls the flow of the gas and a flowmeter 5 measures the flow rate. The gas passes through tube 6 containing sulfuric acid contact catalyst 7, the tube 6 being heated by decomposition reactor 8. In line 9 undecomposed SO_3 and the SO_2 and O_2 products move to condenser 10 where the SO_3 is condensed and returned to evaporator 2 by line 11. The SO_2 and O_2 products continue through line 12 to separator 13 where the SO_2 is condensed, separating it from the O_2 .

Sulfuric acid contact catalysts are a well-known and well-defined group of catalysts. These are catalysts which catalyze the oxidation of SO_2 to SO_3 according to the equation



This oxidation reaction is conducted at relatively low temperatures (<650°C) because at higher temperatures the yield decreases. We have found that the same catalysts will catalyze the reverse reaction, $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$, but only in practical yields at temperatures of 750 to 1000°C. Below 750°C the reaction does not proceed at a significant rate and above 1000°C heat is wasted because no significant increase in reaction rate is obtained. Thus, the temperature range of 750 to 1000°C is to be regarded as critical in this invention.

Examples of sulfuric acid contact catalysts include Fe_2O_3 , V_2O_5 , Pt, including finely divided Pt, platinized asbestos, platinized silica gel, and platinized magnesium sulfate, compounds of chromium, especially Cr-Sn-Ba, Cr-Sn-K, and Cr-Sn, iron, and metal oxides such as CrO, WO_2 , and CuO. The preferred catalysts are V_2O_5 and Pt (usually on a binder or support) due to their relatively low cost, long life, high reaction rate, and high yield. The catalyst should of course be as finely divided as possible.

It is also very important that the SO_2 and O_2 product not be permitted to contact the catalyst at a temperature of less than 750°C once they have formed, in order to prevent their recombination.

As shown in the drawing, the undecomposed SO_3 can be recovered by condensation. It can also be recovered by the addition of water which reacts with it to produce (liquid) H_2SO_4 . The separation of the SO_2 from the oxygen can be accomplished as shown in the drawing by condensation.

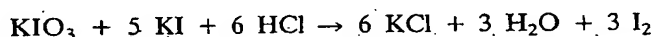
A carrier gas, such as water vapor, may be intermixed with the sulfur trioxide as a result of preceding processes. However, preferably no carrier gas is present as heating the carrier is a waste of energy.

It is necessary that the space velocity be at least 100 hr^{-1} because at lower space velocities an impractically large reaction vessel is required. The space velocity, which is equal to the flow rate divided by the volume of catalyst, is a measurement of the contact time between the sulfur trioxide and the catalyst. Equilibrium conversions at high space velocity means that large quantities of sulfur dioxide can be decomposed quickly in a small vessel. In the process of this invention equilibrium conversion at space velocities of at least $10,000 \text{ hr}^{-1}$ are attainable, which is high relative to most chemical processes.

The invention will now be illustrated by the following Example:

Example

Liquid SO_3 was gradually heated to about 51°C in a three necked round bottom flask. At this temperature its vapor pressure was 3 to 5 psig. Gaseous SO_3 passed vertically from the flask through a check valve and a flowmeter to a differential pressure valve. Beyond this valve, a flow of argon was maintained to purge the equipment following a run and to entrain the SO_3 gas. When the SO_3 and argon gas pressures were equal, SO_3 passed through the valve and was entrained in the argon. A run was initiated by setting the argon flow at the valve to correspond to the space velocity of interest. The volume ratio of argon to SO_3 was 12 to 1. This mixed stream flowed at constant pressure through a reaction tube centered in a split tube furnace which contained a V_2O_5 catalyst ground to -18 to +25 US standard mesh. The SO_3 was decomposed catalytically to SO_2 and O_2 which passed through a three-way stopcock upon leaving the furnace. The gases could then pass through a trap and scrubber series and be vented or they could be bubbled through a sintered glass frit into a stirred aqueous titrating solution containing KI, HCl, and starch. Sulfur dioxide was titrated with 0.1 M KIO_3 . The following equations give the titration reactions.



The SO_2 titration was dynamic and was conducted intermittently while the run was in progress. Titration was maintained just beyond the end point (indicated by a slight blue color). A colorless solution indicated that SO_2 was not being reacted due to lack of iodine in the solution.

Data was obtained by recording the volume of titrant used in a given time period. Six or more such titrating runs were made at each temperature. From the titration reactions and the molarity of the KIO_3 solutions, the number of moles of SO_2 produced per minute, and thus the SO_2 flow rate was calculated.

At a given space velocity the system was purged with argon between the set of runs at each temperature. The volume of catalyst was changed when runs at different space velocities were required.

The first experiments run on this apparatus were to determine the degree of reaction reversal to be expected upon quenching the high temperature gas mixture expected from

the thermal reducer. This information was vital to an interpretation of the thermal reduction rate data taken later. Even more important, however, was the fact that if significant reoxidation of SO_2 occurred following the thermal reduction reaction, the entire process concept would be either useless or highly inefficient.

The degree of reaction reversal to be expected was estimated by passing SO_2 at a constant rate through the reactor, without catalyst present, with N_2 and air carrier gases at various rates. Both hot and cold tests were performed. Under hot conditions, the mixture spent approximately two minutes flowing through the furnace ($500\text{--}1000^\circ\text{C}$) and an additional two minutes in flowing from the 500°C furnace and to the analytical train. Under cold conditions, the gas mixtures traversed the system at room temperature. Residence times lower than four minutes were obtained by increasing the carrier flow while maintaining constant the SO_2 rate.

A statistical analysis of the resultant data indicated identical SO_2 rates into the analytic train for the SO_2/N_2 hot runs and the SO_2/air cold runs. No effect upon residence time, up to four minutes, was observed in the SO_2/air hot runs. Additionally, the SO_2 rate into the analytic train for the hot runs with air at all residence times was identical with that for the cold runs and the inert runs. Since over 100 determinations of SO_2 rate were made during this period, none of which showed any significant statistical departure from the delivery rate, it is certain that SO_2 reoxidation during quench will not be a problem so long as contact catalysts are not present.

The kinetics of the V_2O_5 catalyst was also investigated in the experimental apparatus. The reaction order was determined by testing integrated mass balance and reaction rate equations against the integral reactor data obtained in the system. Once the reaction order is known, the rate constant can be expressed as a function of a reaction group. This group contains a complex function of initial and final sulfur trioxide concentrations and varies with reaction order.

Constructing a mass balance over a differential volume element of the reactor gives

$$F \frac{dx}{dz} = -Acs \cdot r_{\text{rxn}}$$

where

F = volumetric flow rate, cc/hr

x = mole fraction SO_3

Acs = reactor cross sectional area, cm^2

r_{rxn} = rate of reaction, cc/hr multiplied by SO_3 reacted volume

Assuming that the decomposition rate is first order with respect to SO_3 concentration one obtains

$$r_{\text{rxn}} = k_1 C_{\text{SO}_3} = (k_1 C_{\text{SO}_3}^0) x = kx$$

where $C_{\text{SO}_3}^0$ is the initial SO_3 concentration at the reactor inlet.

Substituting yields

$$\frac{dx}{dg} = -\left[\frac{k}{S_v}\right] x$$

where

k = reaction rate const., hr^{-1}

S_v = space velocity = $AcsL/F$, hr^{-1}

g = dimensionless reactor length, Z/L ,

where L = physical length of reactor, and Z = fractional length of reactor.

Using the boundary condition that $x = x_0$ at $g = 0$, the solution becomes

$$\left[\frac{x}{x_0}\right] = e^{-[k/S_v]g}$$

The mole fraction of SO_3 leaving the reactor is given as

$$x_L = x_0 e^{-k_{\text{eff}}/S_v}$$

$$\text{where } k_{\text{eff}} = \frac{1}{\frac{1}{k_g} + \frac{1}{k}}$$

k_g = gas phase mass transfer coefficient

Under conditions of the present investigation, the mass transfer rate was much greater than the rate of chemical reaction, and the effect of k_g can be neglected. The reaction rate constant, k , can be expected to follow the Arrhenius equation, that is,

$$k = Ae^{-E/Rt} \quad 5$$

As a result, the pre-exponential factor, A , and the activation energy E , can be determined from a semilog plot of $\ln(x_0/x_i)$ vs. $1/T$. Under these conditions,

$$\ln[\ln(\frac{x_0}{x_i})] = -\ln \frac{A}{k} - \frac{E}{RT} \quad 10$$

If this model accurately describes the reaction, several predictions can be made. First, a plot on semilog paper of $\ln x_0/x$ vs. $1/T$ should yield a straight line with a slope proportional to E/R and an intercept proportional to (S/A) . Second, the slopes of the lines drawn for all three space velocities should be identical. Only the intercepts should differ. 15

In Figure 2 the ordinate, $\ln(x_0/x)$, is a measurement of the amount of conversion, as hereinbefore explained, and the abscissa is the inverse of the temperature times a thousand. The curves show that the conversion rate increases as the temperature rises.

The top solid line is the calculated equilibrium curve for sulfur trioxide decomposition under the conditions used in these experiments. The points surrounding the top solid line were obtained experimentally at space velocity of $10,000 \text{ hr}^{-1}$. The coincidence of these points with the equilibrium curve show that equilibrium conversion was obtained at that space velocity. 20

The lower curve was experimentally obtained at a space velocity of $60,000 \text{ hr}^{-1}$. Equilibrium conversion was not obtained at that space velocity, but the curve supports the conclusion that the reaction follows first order kinetics. 25

WHAT WE CLAIM IS:

1. A method for the net conversion of gaseous sulfur trioxide into sulfur dioxide and oxygen according to the equation $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$ which comprises passing said gaseous sulfur trioxide over a sulfuric acid contact catalyst at a temperature of 750 to 1000°C at a space velocity (as hereinbefore defined) of at least 100 hr^{-1} ; and preventing sulfur dioxide and oxygen produced from contacting said catalyst at a temperature of less than 750°C . 30

2. A method according to claim 1 which comprises the additional last steps of condensing unreacted sulfur trioxide followed by condensing the sulfur dioxide. 35

3. A method according to claim 1, which comprises the additional last steps of adding water to produce sulfuric acid from unreacted sulfur trioxide followed by condensing the sulfur dioxide.

4. A method according to claim 1, 2 or 3, wherein the catalyst is at least one of vanadium pentoxide and platinum. 40

5. A method, as claimed in claim 1, for the net conversion of gaseous sulfur trioxide into sulfur dioxide and oxygen, substantially as described herein with reference to the foregoing Example and the accompanying drawings.

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COMPLETE SPECIFICATION

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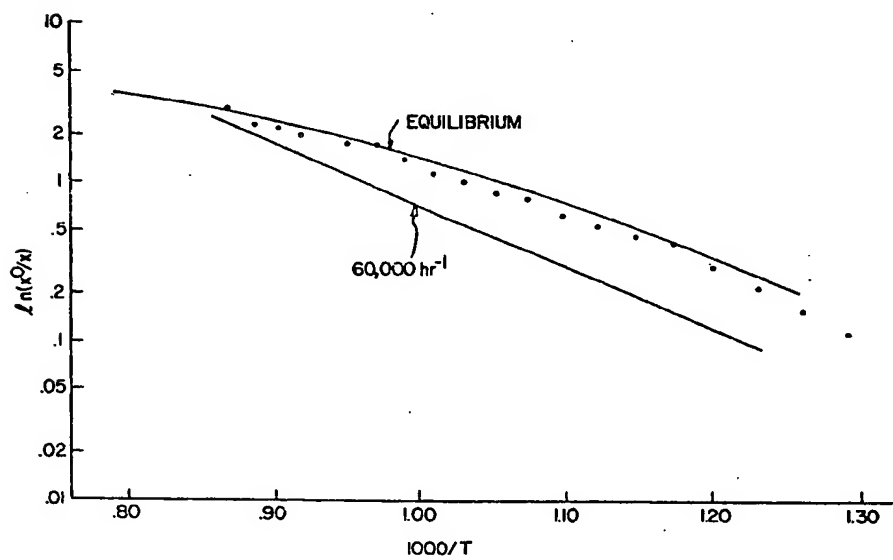
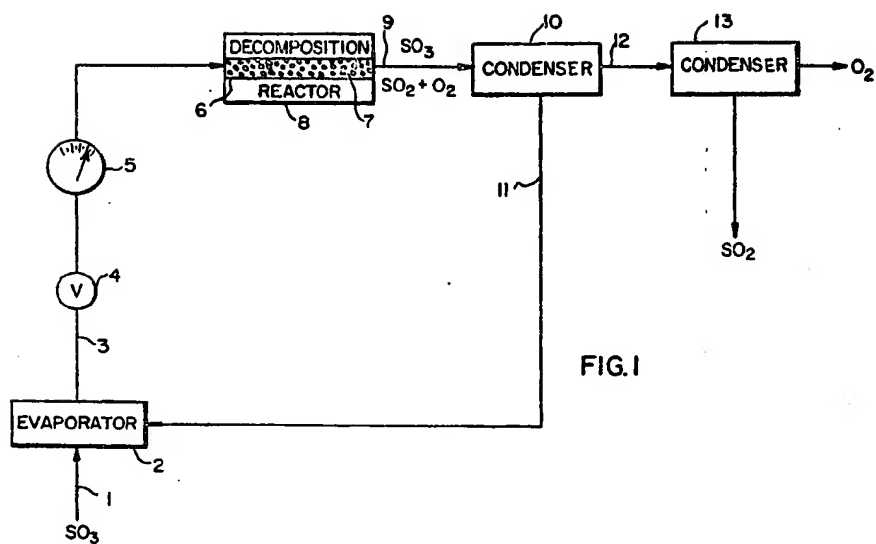
*This drawing is a reproduction of
the Original on a reduced scale*

FIG. 2

